THE ANALYST.

JUNE, 1895.

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS.

The monthly meeting of the Society was held at the Chemical Society's Rooms, Burlington House, on Wednesday evening, May 1. The chair was taken by the President (Dr. Thomas Stevenson).

The minutes of the previous meeting were read and confirmed.

The following gentlemen were elected members of the Society: Mr. H. Irving Foster, The Elms, Anlaby Road, Hull, and Mr. Alec Poole Wilson, Knocklong, Co. Limerick.

Mr. Wynter Blyth then read the following paper:

THE IDENTIFICATION AND ESTIMATION OF CARBOHYDRATES IN MILK.

By A. Wynter Blyth.

The importance of determining in every milk analysis the milk-sugar may be at once conceded, when it is remembered that it constitutes almost a third of the weight of the total solids, that it is the first substance that suffers change by decomposition, and that it is mainly the cause of discrepancies in analyses of stale milks. Experience has also shown that insoluble adulterants are but rarely added to milks; the greatest number are to be looked for in the fluid portion freed from albuminoids and fat. The old method of dissolving out the more soluble portions of milk residues by treating the dried total solids first by ether, and then by dilute alcohol, is both tedious and of small accuracy.

The best method is, after many trials, I am convinced, a physical one, supplemented by a copper process; and lastly, when necessary, obtaining the osazone.

The first step is to prepare a clear whey. An excellent paper on this subject was published so far back as 1887 by Dr. W. Wiley, the chief Chemist for the U.S. Department of Agriculture.* He used the following reagents for the precipitation of the albuminoids:

(1) Saturated solution of basic lead acetate.
(2) Nitric acid solution of mercuric nitrate diluted with an equal volume of water.
(3) Acetic acid, specific gravity 1·040.
(4) Nitric acid, specific gravity 1·197.
(5) Sulphuric acid, specific gravity 1·255.
(6) Saturated solution of sodium chloride.
(7) Saturated solution of magnesium sulphate.

* Foods and Food Adulteration, United States Department of Agriculture, Bulletin No. 13.

(8) Solution of mercuric iodide in acetic acid, a litre of the solution being made with 161 grammes $HgCl_2$, 395 grammes KI, and 228 c.c. of acetic acid.

Dr. Wiley also used a number of other precipitating agencies, but finally gave the preference to two solutions, viz., to the mercuric nitrate, or to the mercuric iodide solution.

These solutions he used as follows: he added 1 c.c. of the mercuric nitrate, or 30 c.c. of the mercuric iodide solution, to certain quantities of milk, varying these quantities according to specific gravity. For a milk of specific gravity 1·026 he took 60·5 c.c. of the milk; if of specific gravity 1·030, 60 c.c. of milk; and if of specific gravity 1·034, 59·5 c.c. of milk. The precipitated albuminoids he considered to occupy a bulk of 2·4 c.c., so that the volume in each case was made up to 102·4 c.c.

The milk thus prepared was shaken, filtered, and the filtrate polarized.

The instrument used by Wiley was a Laurent large model polarimeter. The specific rotatory power of milk-sugar for the sodium light he considered to be 53°.

I have tried both the mercuric nitrate and the mercuric iodide precipitants, and both give good results; but the presence of mercury in the filtrates is objectionable, for the filtrate can only be used for the single purpose of polarimetrical observation. For shadow instruments you can get quite as clear and bright a filtrate from the use of copper sulphate, and if only the proper quantity is taken the filtrate is of so pale a blue that it in no way interferes with the reading; besides which, such a liquid can be treated with Fehling, and the amount of copper suboxide reduced ascertained by weighing.

I have, however, finally adopted a method of precipitating by acetic acid as follows: 25 c.c. of milk are diluted to about 50 c.c. with distilled water, and then strong acetic acid is added drop by drop until the casein begins to separate. The liquid is then heated to boiling, and while still hot, "whirled" in a glass cylinder by the aid of a centrifugal machine. The casein, coagulated serum, albumin, and fat separate and collect in a more or less firm coagulum at the bottom of the cylinder, and the supernatant fluid is easily filtered; the precipitate is also transferred to the filter and washed with hot water. Finally the filtrate is cooled, made up to 100 c.c., and submitted to the processes to be detailed.

The filtrate is usually in a normal milk of a feeble yellow colour, but perfectly bright, and suitable for testing for substances such as salicylic acid, borax, dextrin, or any soluble addition. It is also most suitable for optical methods, and for any estimation of sugar by the reduction of cupric oxide. It will be obvious that such a solution should contain somewhere near 1 per cent. of hydrous milk sugar.

The saccharometer I use is a Laurent half-shadow arranged for ordinary white light, and the source of illumination has been a "Welsbach" incandescent gas-flame. The saccharometer has a straight index with vernier, and 100° on the scale is equal to a 16·2 per cent. of sugar when viewed in the 20 centimetre tube. The optical power of sugars generally is not the same for strong as for dilute solutions, so that as a 1 per cent. solution is in all these cases taken, it is essential that the instrument be standardized with the same solution as is used for standardizing the copper process. For example, in my own instrument, 10·28 per cent. milk-sugar in a 400 m.m. tube marks 100° on the scale, but a 1 per cent. marks 10°; similarly, 1 per

cent. of cane-sugar, or 1 per cent. of dextrose, all have for such dilute solutions a slightly different value at ordinary temperatures—from 15° up to 18°—than stronger solutions.

If cane-sugar is large in amount relatively, the optical supplemented by the copper process at once reveals it, for we have in this case two sugars, both having an action on polarized light in different proportions, and the one having an action on copper, the other but little action on copper. Thus, a milk which was prepared so as to have practically equal parts of cane and milk sugar, containing in 100 c.c. 3·48 of cane-sugar and 3·52 of milk-sugar, gave by the saccharometer an indication of 8 per cent. of milk-sugar; by copper an indication of 3·9 per cent. of milk-sugar, so that, without inversion, it would be evident that in this case a sugar was present that rotated strongly, and only acted on copper slightly; and dextrin having been proved absent by testing the clear liquid with iodine, there would not be much error in diagnosing the presence of cane-sugar.

With smaller proportions of cane to milk, the differences are not so great, and inversion is necessary. Inversion of the whey of pure milks, calculated, not into galactose, but lactose, makes an apparent difference of from 0·5 to 0·8 per cent.; thus, a milk which by the optical method showed 4·11 per cent. of milk-sugar, and by copper 4·23 per cent., on inversion (by HCl) showed 3·5 per cent. milk-sugar at 16°.

This change in the optical power of milk-sugar on inversion with HCl renders the ordinary method of calculating the proportion of cane-sugar in these dilute solutions inapplicable.

Nevertheless, as a means of diagnosis inversion is valuable. A milk was prepared containing in 100 c.c. 3·73 per cent. of milk-sugar and 0·89 per cent. of cane-sugar.

In the 400 m.m. tube of my instrument, this should rotate, when diluted as in the process given, as follows:

0·93 of milk-sugar	9·3 degrees
0·27 of cane-sugar should mark	2·00 degrees
	11·3

The actual degrees found were, however, a little higher, viz., 11·7, and this would be considered to be equal to 4·68, or, say, 4·7, of milk-sugar; copper indicated 5·0 per cent. of milk-sugar; on inversion, the copper value rose to 6·6 per cent. of milk-sugar, and the polarimetric reading at 18·0 was 6·3 degrees, showing a reduction of 5·42 degrees.

If glucose be added to milk, we then have the problem of two sugars, which act unequally to polarized light and which act unequally towards copper, thus, with the same proportions as in the last case, that is to say, or nearly so, on a milk containing 0·9 glucose and 3·73 milk-sugar, the saccharometer indicated 4·4 milk-sugar, and the copper 6·2, a difference between the optical and the copper processes of 1·8 per cent.

The Determination of Sugar by Copper.—In my earlier experiments, this was done by weight, a known quantity of the filtrate being boiled up with an excess of Fehling, the hot liquid transferred to a cylinder, well "whirled," the supernatant fluid being decanted, the copper suboxide washed by decantation with hot water until the water was no longer alkaline, and then the cylinder with the copper oxide dried and weighed.

In this way the difficulty of filtration was avoided, and the method was fairly speedy, and good results were obtained; the difference between the two determinations expressed as milk-sugar varying from 0·1 to 0·19 per cent.

Since, however, the publication by Mr. Gerrard* of his improved cupric cyanide process, the determination by weight has been abandoned, and the milk-sugar is estimated as follows: To 10 c.c. of a copper solution (Fehling's strength) 10 c.c. of the alkaline tartrate are added, and the liquid still further diluted with 40 c.c. of water, heated to boiling, and then drop by drop a 5 per cent. solution of potassic cyanide added, until there is only the faintest blue colour to be observed. A second quantity of copper and alkaline tartrate is then added, and, while boiling, the same 1 per cent. solution of milk-sugar, diluted one half, which has been used for standardizing the saccharometer, run in slowly from a burette to complete decolorization. Having made two or more experiments with the pure solution of known strength, it is obvious the value of the Fehling in terms of milk-sugar is accurately known; 50 c.c. of the already diluted milk-whey are made up to 100 c.c., and this is run into the boiling Fehling as before until the blue liquid is decolorized. The end reaction is quite definite and sharp. Soxhlet has laid it down that, as regards the ordinary determination by Fehling of milk-sugar, complete reduction does not take place under some six minutes' boiling. This observation does not apply to the cupric cyanide process; the decolorization attains its maximum for a given quantity of milk-sugar solution of the strength named well within a minute and a half.

The following table gives an example of a few milks which have been "whirled," the fat determined by the centrifugal machine, the specific gravity taken by a hydrometer, the total solids calculated by the Richmond scale, and the milk-sugar determined both by copper and by the polarimeter:

Analyses of Commercial Milks.

Specific Gravity.	Total Solids.	Fat.	Milk-sugar.	
			Polarimeter.	Cyanide Copper Process
1031	10·4	2·2	4·08	4·31
1034	12·68	3·5	5·00	4·90
1032	11·1	3·0	4·24	4·31
1033	12·9	3·8	4·24	4·26
1032	12·3	3·6	4·04	4·56
1034	12·55	3·4	4·40	4·24
1033	11·85	3·0	4.24	4·23
1033	12·78	3·8	4·72	4·92
1031	11·8	3·4	4·20	4·26

Hence, it is abundantly clear that, should there be an appreciable difference between the presumed percentage of milk-sugar, as determined by optical and copper processes, the carbo-hydrates of the milk are abnormal, and there is a probability of either dextrin or cane-sugar, or glucose, having been added, and it is necessary to examine further.

Dextrin may be dismissed in a sentence, for the clear filtrate, when tested with a

* *Pharm. Journal*, 3rd Series, vol. xxv., 912.

droplet of iodine, at once gives the well-known reddish colour, so that its qualitative detection is as simple as possible.

To identify with certainty foreign sugars, it is well to obtain the osazone. Twenty-five c.c. of the milk are diluted, as previously described, and a filtrate obtained, free from serum albumin casein and fat, neutralized and concentrated down to 30 c.c. During this process an albuminoid settles and adheres to the bottom of the dish, which is separated by filtering through a very small filter ; to the clear filtrate 2 grammes of sodic acetate and 1·5 grammes of phenylhydrazin hydrochlorate are added, and the whole heated in a flask in a water-bath for one hour and a half. On cooling, the liquid becomes almost solid : the crystalline magma is collected on a filter, washed once with a little cold distilled water ; the crystals are pressed between blotting-paper and dried in a water-oven. The osazone is then boiled with absolute alcohol, just sufficient to dissolve it ; this, for the quantity taken, is usually about 30 c.c. to 40 c.c. ; the alcoholic liquid is allowed to stand over night to see if any crystals separate. Should glucose or invert sugar have been present, well-defined crystals will have separated ; if milk-sugar alone was present, there may be a slight amorphous deposit at the bottom of the flask, but no crystals visible to the unassisted sight.

The purification of the lactosazone is now proceeded with. The alcoholic solution is placed on the water-bath and heated to boiling, and while boiling hot water is added little by little until a slight turbidity shows itself ; a good portion of the alcohol is now allowed to evaporate slowly away, and on placing the liquid in a cool place the osazone crystallizes out. Lactosazone derived from such a precipitation is coloured, and, microscopically examined, is seen to consist of aggregations of warty masses, some of which are strikingly like starch granules, exhibiting a split hilum with radiating fissures ; this appearance is constant and characteristic, but it is also a sign that the osazone is not pure. Such crystals melt at various temperatures, according to purity, from 190° to 195°. To obtain it pure, the process of dissolving in alcohol, precipitating by hot water, pressing the crystals between blotting-paper, drying, etc., will have to be done at least three times. When pure the crystalline appearance is very similar, but not identical to that of glucosazone, viz., needle-like crystals—these melt at 200° or a little above. Since one of the main methods of distinguishing between the osazones is their solubility or insolubility, I have made a few observations on the solubility of lactosazone.

If lactosazone is shaken up with water and allowed to stand for twenty-four hours, then 100 c.c. of water dissolves 20 milligrammes. If 14 c.c. of a saturated solution in alcohol be poured into 100 c.c. of water and allowed to deposit, every 100 c.c. of the filtered solution hold in solution 34·8 milligrammes. Lactosazone is freely soluble in hot alcohol, and none separates on cooling, unless the solution be highly concentrated.

On the other hand, glucosazone requires repeated boiling in considerable quantities of absolute alcohol before it dissolves, and on cooling most of the osazone separates out 100 c.c. of 98 per cent. alcohol, only retaining, at ordinary temperatures, 30 milligrammes.* The separation is in fine crystals. These crystals, without further purification, melt at or about 197° ; while, as before remarked, the impure osazone from

* 100 c.c. of cold water only retain 11 milligrammes of glucosazone in solution.

milk-sugar melts from 190° to 195°; glucosazone can therefore be rapidly purified by two or three crystallizations from alcohol; it then has a melting-point of 203° to 204.° Glucosazone is always in the form of needles, most of which are in bundles. No warty or starch-like appearance has been observed. A mixture of glucosazone and lactosazone may be separated in great part by fractional crystallization.

Cane-sugar gives no osazone until inverted; it then gives an osazone not to be distinguished from glucosazone; so that the diagnosis of a milk adulterated with cane-sugar is:

(1) The considerable want of agreement between the results from the copper process and the polarimeter readings.

(2) Lactosazone is alone obtained by treatment with phenylhydrazin.

(3) On inversion the considerable rise in the amount of copper reduced.

ADDENDUM.—Since I had the advantage of hearing the discussion on the foregoing paper, I have had made by my assistant, Mr. W. A. Rogers, a few experiments on the citric acid method of inversion. Fifty c.c. of a 1 per cent. solution of milk-sugar gave an optical value in the 400 m.m. tube of 10·1°, and 6·3 c.c. decolorized the hot cupric cyanide. On heating to boiling for nearly twenty minutes the same solution with half a gramme of citric acid, replacing the evaporated water until it assumed its original bulk at 15°, the optical value was unchanged, and the c c. used to decolorize the copper were 6·6, so that I conclude that no change took place in the milk-sugar. On the other hand, 100 c.c. of a 1 per cent. solution of milk-sugar acidified with 2 grammes of citric acid, and concentrated down to 30 c.c. on the water-bath, suffered change, and a portion was converted into galactose; a small amount of a crystalline osazone was separated, which, after several crystallizations, melted at 197·5°, and was probably not quite pure galactosazone.

A hundred c.c of 1 per cent. solution of cane-sugar was rapidly inverted by the addition of 1 gramme of citric acid and heating for 20 minutes.

Fifty c.c. of a 1 per cent. solution of milk-sugar and 50 c.c. of a 2 per cent. solution of cane-sugar mixed, gave, before inversion, an optical value of + 16·25°; after inversion with citric acid an optical value at 18° of + 3·6°. Before inversion the number of c.c. consumed of the solution to decolorize the copper was 14·2; the number after, 3·8 c.c. Hence without a doubt the citric acid method promises well, and if the acid is not added in excess and the heating not prolonged, the milk-sugar is not affected.

DISCUSSION.

The President having invited discussion,

Mr. RICHMOND said that his experience had led him to prefer Dr. Vieth's modification of Dr. Wiley's method of preparing the whey, as being more accurate. One great advantage of this method was, that the fact of the mercuric nitrate being added in the proportion of 3 c.c. to 100 c.c. of the milk caused the whey to occupy the same volume as the original milk less that of the fat, since, for all practical purposes, 3 c.c. might be taken as the volume of the albuminoids precipitated.

With regard to polarimeters, he had found that the instrument described and used by Dr. Vieth gave sufficiently good results, and its price was very much lower than that of the instrument mentioned by Mr. Blyth. As the former instrument was

in the possession of a good many analysts, he would like to point out a small error occurring in Dr. Vieth's description of it. It was stated that the instrument might be taken as reading the percentages of milk-sugar direct; this, however, was only true speaking broadly; to be more accurate, the reading should be divided by 1·042. If, however, Mr. Blyth's plan of standardizing from a solution of known strength were adopted, this discrepancy would not be found.

He thought it might be useful, in estimating sugar other than milk-sugar, to bear in mind the ratio—pointed out many years ago by Dr. Vieth—between the ash, albuminoids and milk-sugar, viz., 2 : 9 : 13, which had been found to hold good to an extent that might almost be called remarkable. For the estimation of cane-sugar there was Kjeldahl's process of inversion by means of invertase, which only affected the cane-sugar, and not the milk-sugar, so that if a solution were made and treated with invertase, and any change in the rotating powers was observed, it might be regarded as certain that cane-sugar was present.

Mr. Blyth relied on the separation of the osazones for the detection of glucoses, but the anhydride of phenyl-lactosazone (lactose being the only sugar which gave an anhydride) would probably interfere with this reaction.

Mr. Allen said that, many years ago, before the value of the solids-not-fat was recognised, it was his custom to determine the specific gravity of the whey of milk. For this purpose about 100 cc. of the sample were heated to about 120° C., and then five or six drops of acetic acid added without agitation. On keeping the liquid at rest for eight or ten minutes the curd separated perfectly, so that with care nearly the whole of the whey could be syphoned off. If once the liquid was agitated, it was found impossible to obtain a clear filtrate.

He (Mr. Allen) had made a number of experiments with Gerrard's cyano-cupric process of titrating glucose. In its original form the method was quite unworkable, but the improved process, described in the *Pharmaceutical Journal* for April 20, which he might say was practically worked out jointly by Mr. Gerrard and himself, gave excellent results. He regarded this as the best of the copper methods of titrating glucose, but had had no experience of it in the titration of milk-sugar, and should like to be quite sure that the same ratio of reduction applied as in the ordinary Fehling's or Pavy's test before he accepted the indications of the process as correct.

In working with the osazones, he had observed that glucosazone could be readily extracted from acidulated aqueous liquids by agitation with ether, which fact might be used for its purification.

Mr. Wynter Blyth stated in his paper that he detected cane-sugar in presence of milk-sugar by boiling the mixture with dilute acid, which converted the former sugar into a mixture of dextrose and lævulose, and the latter into galactose. He then separated these by taking advantage of the different solubilities of their osazones in alcohol. But this process entirely ignored the fact that dextrose was a product, together with galactose, of the inversion of milk-sugar, and this circumstance entirely vitiated the process, since the same osazone would be produced both from cane-sugar and from milk-sugar. A far more hopeful plan would be to invert the cane-sugar by citric acid, as proposed by Messrs. Stokes and Bodmer some years since, as this reagent left the milk-sugar unchanged.

Mr. Bodmer said that the method of inverting with citric acid was, he believed, one of the simplest available for the estimation of cane-sugar in milk. It was quite possible to prove whether a sample of milk contained, say, 0·5 per cent. of cane-sugar in about twenty minutes. The milk was coagulated in the way described in the paper (except that citric acid was used instead of acetic), made up with alkali, and titrated with Pavy's solution. Another portion of the same solution was inverted by boiling with citric acid, neutralized and titrated, the increase in reducing power being due to cane-sugar.

Mr. Hehner thought that the use of acetic acid as a precipitant was a retrograde step. Although it removed by far the larger proportion of the albuminoids, it left behind nitrogenous substances of high rotatory power, the presence of which would affect the results.

He would like to ask Mr. Blyth if he had ever in actual practical work met with a milk containing any carbohydrate besides milk-sugar.

Mr. Bevan inquired what was the smallest quantity of cane-sugar that could be accurately determined by the methods employed by Mr. Blyth. He believed that in Mr. Blyth's book it was stated that it was useless to attempt to determine cane-sugar unless it could be distinctly tasted.

The method of separating the albuminoids by means of acetic acid was in operation in the French municipal laboratories, although the details of its application were somewhat different. They used a ribbed filter, pouring in first 200 c.c. of very dilute acetic acid, and then from 10 to 20 c.c. of the milk. After a few minutes the tap at the bottom of the funnel was opened, and the filtrate allowed to run through. The sugar in the filtrate was estimated by means of copper solution, as it was too dilute for the polarimeter. The residue—allowed to dry spontaneously—was an excellent preparation for estimating the fat, the ribbed filter being placed in a Soxhlet and treated with ether.

Mr. Cassal said he thought the only recorded case of a sample of milk adulterated with sugar and submitted officially to a public analyst was one given to the Society by Dr. Muter, who had determined the milk-sugar and added sugar.

In precipitating condensed milk—which was necessary in order to make an accurate determination of the fat—he had found that sulphate of copper gave very satisfactory results.

Mr. Wynter Blyth said he agreed with Mr. Richmond that mercuric nitrate, as a precipitant only, possessed certain advantages, but the filtrate could not be used for any other purpose, which was a great disadvantage. It might, of course, be possible to invert successfully in a filtrate in which a salt of mercury was present, but he thought it preferable that there should be as little foreign matter as possible in the filtrate. He had been disappointed with cheap polarimeters. His experience led him to think it worth while paying a little more, and getting a really serviceable instrument which could be relied upon.

He had never made use of invertase. As a matter of fact, this investigation was not at all complete, it having been interrupted by numerous engagements of one kind and another, but he ventured to hope that the discussion it had raised might be considered a useful outcome of the paper as it was.

He had not been aware of the fact stated by Mr. Allen of the solubility of the osazones in ether.

From Mr. Bodmer's remarks he imagined that the citric acid process would be very useful, although he had not as yet availed himself of it.

He did not think that less than about $\frac{1}{4}$ per cent. of cane-sugar could be certified to with absolute confidence. In reply to a further question by Mr. Bevan, he said that all milk samples passing through his hands were now tested with the polarimeter, but this had only been done for a very short time as a matter of routine, which would account for his being unable to say that he had ever met with a sample adulterated with cane-sugar in actual work.

The PRESIDENT said that they were much indebted to Mr. Blyth for this paper; anything which added to what was known regarding the relationship between the various constituents of milk was not only of interest to public analysts, but formed a substantial advance in scientific chemistry.

Papers were read on the following subjects: "A Comparison of the Organic Carbon and Nitrogen Results obtained by Dr. Frankland and the Companies' Analysts from the Waters supplied by the Metropolitan Water Companies," by W. C. Young; "Note on the Detection of Formalin in Milk Samples," by S. Rideal, D.Sc. The publication of these is unavoidably postponed.

NOTES ON CINNAMON.

By BERNARD DYER, D.Sc., AND J. F. H. GILBARD.

(*Read at the Meeting, February* 6, 1895.)

ONE of us was lately informed that a certain firm of confectioners abroad, who did a heavy trade in walnuts, which they used in various forms for confectionery, had a large sale for their walnut-shells—in fact, that they sold them in London for more than they gave for the whole walnuts, the shells being used in adulterating ground cinnamon.

As, in addition to this statement, information to somewhat the same effect was made public, it appeared likely that ground cinnamon might receive the attention of food inspectors; and as it also appeared that little information was available about either cinnamon or ground walnuts, some typical samples were obtained from Messrs. Joseph Travers Sons, Limited, representing "cinnamon chips," "broken cinnamon," and three kinds of "quill cinnamon," two of ordinary and one of a "superior" variety. We examined these, and also a sample of finely-ground walnut-shells.

The microscopic detection of powdered walnut-shells in ground cinnamon is not difficult to a skilled observer; but an inexperienced microscopist might well be misled if he did not very carefully study both structures. Cinnamon-bark contains a large proportion of very hard sclerenchymatous tissue, the dense, internally thickened cells of which are, but for size, not wholly dissimilar from the sclerenchyma con-

stituting the harder portion of the walnut-shell. Any microscopical observation made with a view to the detection of walnut-shells should not be undertaken, therefore, without a careful independent study of the microscopical structure of cinnamon-bark itself, as well as of the supposed adulterant.

Assuming that the microscopical examination gives evidence of the presence of ground walnut-shells, the question of estimating the quantity present has to be met; and it is with a view to furnishing data for such purposes that the analyses were made which resulted in the following figures.

"Approximate Volatile Essential Oil" merely means the difference between the ether extract lightly dried on the top of the water-oven and the fixed ether extract obtained by complete drying inside the water-oven; the figure, in fact, being comparable to that given for "Approximate Volatile Essential Oil" in our previous paper on "Ginger."

"Fixed Ether Extract" is the non-volatile portion of the matter extracted by repeated exhaustion with ether until no more can be obtained.

"Alcoholic Extract after Ether" is the whole of the matter removable by prolonged exhaustion with alcohol in a Soxhlet apparatus after the removal of the ether extract.

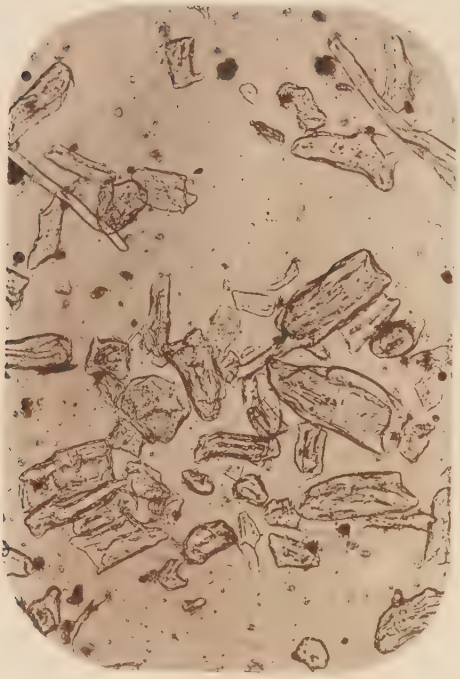
"Fibre" is woody fibre obtained in the same way as in a feeding-stuff analysis.

	Moisture (Loss at 100° C.).	Approximate Volatile Essential Oil.	Fixed Ether Extract.	Alcoholic Extract after Ether.	Total Ash less Sand	Ash soluble in Water.	Ash insoluble in Water.	Fibre.	Nitrogen.
Cinnamon chips ...	12·57	0·77	2·10	12·43	3·96	0·19	3·77	34·10	0·50
Broken cinnamon ...	11·33	1·53	2·30	12·90	4·80	0·10	4·70	34·33	0·54
Quill cinnamon (*a*) ...	13·00	1·87	2·13	13·27	2·97	0·90	2·07	35·67	0·54
Quill cinnamon (*b*) ...	12·50	1·77	1·87	11·00	4·40	0·63	3·77	34·27	0·42
Quill cinnamon "superior" ...	12·65	1·93	2·30	13·23	5·00	0·50	4·50	32·90	0·54
Average of these five samples ...	12·41	1·57	2·14	12·57	4·22	0·46	2·76	34·25	0·51
Ground walnut-shells	9·97	0·27	1·60	3·67	0·87	0·37	0·50	47·67	0·20

The items "Volatile Oil," "Alcoholic Extract," "Insoluble Ash," and "Nitrogen" would all be obviously of assistance in calculating the percentages in a mixture of ground cinnamon and walnut-shells.

The fixed ether extract is not of much value for such purposes, and the soluble ash varies so greatly as to be of no use at all.

1.



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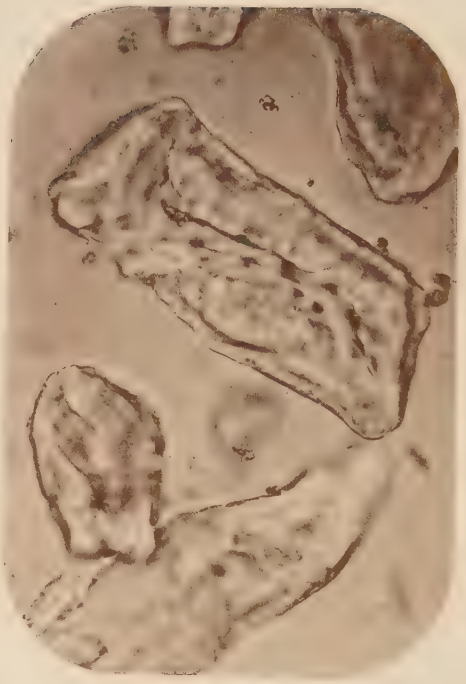

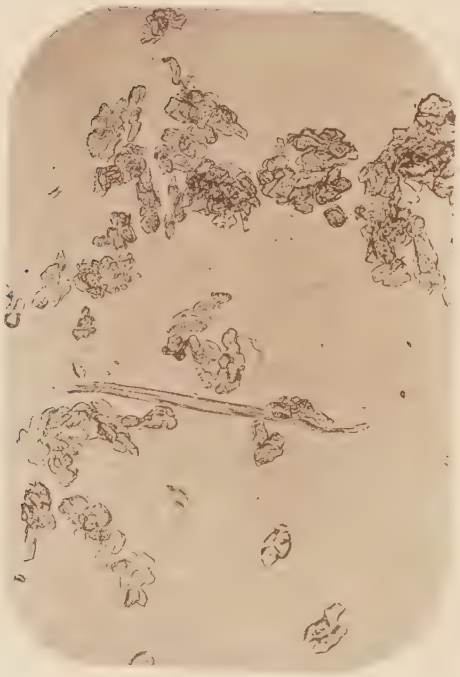

3.

4.

The woody fibre in cinnamon is pretty constant, and is appreciably less than in walnut-shells.

ADDENDUM.

The accompanying micro-photographs show the appearance, under high and low powers of the microscope, of bleached schlerenchymatous cells prepared by ourselves from both cinnamon and walnut shells.

No. 1, cinnamon under a low power; No. 2, ditto, more highly magnified; No. 3, walnut shells under a low power; No. 4, ditto, more highly magnified.

The photographs were very kindly made by Mr. A. Ashe, and have been reproduced by Messrs. Waterlow and Sons.

CRYSTALLIZED GLYCERIN.

(*Meeting, April* 3, 1895.)

Mr. Bevan exhibited some specimens of crystallized glycerin. He said that some time back a sample of glycerin had been submitted to him, which consisted of a mass of small crystals resembling soft sugar. He had found that by dropping a small quantity of the crystals into ordinary glycerin kept at a temperature of about 15° C., fresh crystals could be grown at a considerable rate.

DISCUSSION.

The Chairman (Mr. Otto Hehner) thought that, since commercial glycerin was not anhydrous, the glycerin above the crystals (unless the crystallized glycerin was a hydrate, which he believed was not the case) would become more and more dilute as the crystallization increased. It was remarkable that glycerin should crystallize out of an aqueous solution, since it was only anhydrous glycerin that was supposed to crystallize.* This seemed to suggest that glycerin was a crystalline substance in a state of supersaturation, the occasional upsetting of which showed the glycerin in its true state.

He would like to know whether an actual crystal was absolutely necessary to start the crystallization, or whether anything else would serve as a nucleus.

Mr. BEVAN said that the glycerin above the crystals, or mother-liquor, so to speak, was weaker than the original glycerin, and of course much weaker than the crystals. The case was different, however, from that, for instance, of water, which, when cooled down below its congealing point, crystallized in a solid mass the instant it was touched, whereas, in the case of glycerin, the process required a considerable time.

He had never been able to obtain crystallization except by starting with an actual crystal. Professor Dewar had obtained glycerin in a solid mass resembling glass, by cooling with the aid of solid carbonic acid and ether.

* Since speaking, I have analysed both crystals and mother-liquor. The former are pure anhydrous glycerin; the latter contains 6 per cent. of water.—O. H.

Mr. Bodmer said that a sample of glycerin existed some years back in the dispensary at Guy's Hospital, which was absolutely solid. There was no mother-liquor at all, the material being exactly like a piece of ice.

THE COMPOSITION OF SOME ENGLISH CHEESES.

By W. Chattaway, T. H. Pearmain, and C. G. Moor, M.A.

(*Read at the Meeting, April* 3, 1895.)

In the July number of The Analyst of last year we published some figures representing the composition of several different kinds of cheese, and as we have recently been supplied with a series of specimens of English manufacture, we think the figures worth placing on record, particularly as they have all been made under proper scientific supervision and regulated conditions.

Some of them are imitations of foreign cheeses, and appeared to us to compare favourably with those made abroad.

With regard to the estimation of fat in cheese, after having paid some considerable attention to the question, we prefer the following process :

50 grammes of the cheese are ground up in a mortar with a fairly large quantity of sand. The powder so obtained is placed in a tall stoppered cylinder, and extracted by means of four successive portions of ether, using in all about 500 c.c. The ether washings are then made up to a definite volume, an aliquot portion taken, and the ether removed in the usual way. The residue of fat can then be subjected to further treatment in order to prove that it is true milk-fat.

When it is merely necessary to estimate the fat, this can be quickly and accurately done by means of the following modification of the Leffmann and Beam process for milk.

2·0 grammes of the cheese are taken, reduced to as fine a state of division as possible, then transferred to a small dish and treated on the water-bath with 30 c.c. of concentrated hydrochloric acid until solution is effected, and the fluid assumes a dark purplish colour. The mixture is now poured into a Leffmann-Beam bottle, the dish rinsed with the hydrochloric acid fusel-oil mixture into the bottle, and, finally, enough strong hot acid added to fill the bottle up to the mark. It is then centrifugated for about one minute. The Leffmann-Beam bottles are graduated so that ten divisions equal 1·0 per cent. by weight of fat on the 15·55 grammes of milk taken.

It follows, therefore, that the factor to be made use of in this case will be :

$$\frac{15{\cdot}55}{2} = 7{\cdot}7$$

With very little practice concordant readings are easily obtained, which agree very closely with the extraction process already explained.

We estimate the nitrogen by the Kjeldahl method, but find it essential to use a capacious distillation head in order to obviate the great inconvenience caused by the frothing which generally occurs when estimating the nitrogen in cheese by this process.

Name of Cheese.	Fat.	Water.	Ash.	Nitrogen.	Proteids N × 6 3.
Port de Salut	36·2	31·3	4·6	4·2	26·5
Caerphilly	30·4	24·8	3·4	5·9	37·2
Culommier	24·1	37·8	4·1	3·9	24·6
Cleveland	35·0	38·0	3·4	4·4	27·7
Cambridge	47·1	32·1	4·4	3·9	24·6
Gorgonzola	33·2	33·5	3·5	6·0	37·8
Double cream	68·1	14·0	1·2	3·2	20·1
Camembert	33·2	35·0	2·9	5·5	34·6
Gervais	69·3	15·8	0·6	3·0	18·9
Wensleydale	33·3	28·3	3·7	4·3	27·2
Cheddar	30·5	37·7	3·9	4·6	29·0
Stilton	34·6	25·0	4·1	4·5	28·4

Discussion.

Mr. Allen drew attention to the large differences between the amount of fat in the various cheeses, remarking that it was at the same time rather striking that all the figures for fat, excepting for the Cheddar, were over 35 per cent. He believed that the authors had mentioned in a previous paper a Dutch cheese containing only 10 per cent. of fat. These differences emphasized very strongly the obstacles with which the fixing of standards was beset, and the difficulty of laying down limits which should ensure equal justice to the trade and to the consumer. It was well to keep a watch upon cheeses containing very small proportions of fat, although it might not be advisable at present that such should be absolutely condemned. It was very desirable that as complete data as possible should be placed on record regarding the composition of articles of food as arrived at by modern methods, and he thought the authors of the paper had done good work in this direction.

Dr. Voelcker said that he should have expected to find a greater difference between the percentages of fat in Stilton and Cheddar cheese than the 4 per cent. indicated in the table. It was the practice in making Stilton cheese to add a considerable amount of cream, and this would result in an excess of fat over that in the Cheddar—which was an ordinary cheese, and not a cream cheese—of considerably more than 4 per cent.

Dr. Rideal said that as the amount of nitrogen as determined would probably in most of the cheeses indicate, not only proteids, but also ammonia and other decomposition-products, it was as well to calculate the exact relation between the nitrogen and the proteids for each cheese.

Mr. Bevan said that in the case of the first three cheeses in the table, if the proteids were taken at $6\frac{1}{4}$ times the nitrogen, the figures added up to just under 100. In the case of Gorgonzola the sum of the figures came to 107·7, but an error of something over 1 per cent. in the nitrogen determination would account for this. He did not, of course, mean to imply that $6\frac{1}{4}$ was necessarily the right number, but it was interesting to note that the figures obtained by using it agreed very well in most of the cases.

The Chairman (Mr. Otto Hehner) pointed out that the authors had only dealt with cheeses of English make, and that the composition of the English-made imitations of foreign cheeses should not be taken as affording information as to the composition of the "genuine" articles.

Cheese analyses ought not to be expected to add up to 100, as multiplication of the nitrogen by $6\frac{1}{4}$ to obtain the proteids assumed that the nitrogen existed in the form of albuminoids only, which was not the case, especially in Gorgonzola and similar cheese, which contained a proportion of nitrogenous basic substances.

With regard to standards, in America the conclusion had been reached that at least 40 per cent. of the total solids in genuine cheese should consist of fat. Seeing that in normal milk the fat was about equal in amount to the albuminoids, one half of the total solids in cheese ought to be fat, although this was frequently not so, even in what would be called good cheese. In England, cheese made from skimmed milk, provided that it contained no fat other than milk fat, was passed as genuine, which was unfair to the manufacturers of whole milk cheese. In the case of milk, the sale of skimmed milk, when milk was asked for, was illegal, and skim-cheese ought to be on the same footing.

Mr. C. G. Moor said that they had hardly expected the nitrogen determination to escape criticism, as the separately determined constituents did not add up quite so close to 100% as might have been wished for. The factor 6·3 did not always answer, although he could not think that this was due to the formation of ammonia, as the samples were all perfectly fresh when examined.

The imitations of foreign cheeses had all been made under as nearly as possible the same conditions as prevailed abroad, from the same materials as the originals, and in the same proportions.

THE TESTING OF OILS WITH THE OLEO-REFRACTOMETER.

By Thomas H. Pearmain.

(*Read at the Meeting, April* 3, 1895.)

Now that the oleo-refractometer, as devised by Messrs. Jean and Amagat, is coming so largely into use in commercial work, the following table, which gives a summary of the results of the examination of 240 samples of oil, may be of interest.

I find much better results are obtained with this instrument when the temperature is falling, especially in the case of butter and margarine, which, owing to their higher melting-point, have to be observed at the higher temperature, namely, 45° C.

If the sample of oil under examination is very acid, it is necessary to remove the free fatty acid by shaking the oil in a separator with hot alcohol, after which treatment the oil is dried at 105° C.

In testing oils which give a high deviation, as the fish oils, for instance, it is desirable when making the observation to dilute them with their own volume of lard-oil, whereby a much sharper shadow is obtained. The figure so obtained is, of course, doubled to obtain the proper refraction number of the oil.

It is to be regretted that the oleo-refractometer is not a more satisfactory test in the case of butter and margarine. My results confirm those of G. H. Ellinger (The Analyst, 1891, p. 197), who tested 510 samples of Danish butter, and found the greatest difference of deviation to be from 35°-23° when examined in this instrument at 45° C.

Temperature 22° C.	Number of Samples Examined.	Deviation.	Highest.	Lowest.	Average.	Temperature 22° C.	Number of Samples Examined.	Deviation.	Highest.	Lowest.	Average.
Almond ...	8	+	10·5	8·0	9·5	Poppy-seed ...	3	+	35·0	30·0	33·0
Arachis (Earth Nut) ...	5	+	7·0	5·0	6·0	Rape	8	+	20·0	16·0	17·5
Bottlenose ...	1	+	50·0	50·0	50·0	Ravison ...	2	+	24·0	20·0	22·0
Cabbage Seed...	1	+	15·0	15·0	15·0	Seal	2	+	36·0	30·0	33·0
Castor	8	+	42·0	39·0	40·0	Sesamé ...	5	+	17·0	13·0	15·5
Cod-liver ...	8	+	46·0	40·0	44·0	Shark	3	+	35·0	29·0	31·0
Cotton-seed (Crude) ...	3	+	17·0	16·0	16·5	Sunflower ...	1	+	35·0	35·0	35·0
Cotton-seed (Refined) ...	6	+	23·0	17·0	21·5	Tallow Oil ...	2	−	5·0	1·0	3·0
Hempseed ...	4	+	37·5	34·0	35·5	Tea	1	+	8·0	8·0	8·0
Japan-wood Oil	1	+	75·0	75·0	75·0	Whale	2	+	48·0	42·0	45·0
Lard Oil ...	6	−	1·0	0·0	0·0	Oleic Acid ...	3	−	33·0	29·0	32·0
Linseed (Crude)	3	+	52·0	48·0	50·0						
Linseed (Refined) ...	5	+	54·0	50·0	52·5	Temperature 45° C.					
Neat's Foot ...	2	−	3·0	1·0	2·0	Butter	15	−	34·0	25·0	30·0
Niger-seed ...	2	+	30·0	26·0	28·0	Margarine ...	7	−	18·0	13·0	15·0
Olive	105	+	3·5	1·0	2·0	Lard	10	−	14·0	8·0	10·5
Peach Kernel...	2	+	11·5	7·5	9·5	Tallow	6	−	18·0	15·0	16·0
Pilchard ...	2	+	36·0	32·0	34·0	Paraffin (Soft)...	2	+	58·5	54·0	56·0

Discussion.

Mr. Bevan said that it was his practice to examine with the oleo-refractometer every sample of butter passing through his hands, and he had never found it lead to a mistake. Its working, however, depended to some extent upon the personal element, as well as upon the exact position of the prism, and there might be differences between the results of different observers using different instruments.

He suggested a mixture of glycerine and water as a substitute for the standardizing oil supplied with the instrument. It would be much cheaper, and would be free from the disadvantage of being only obtainable in Paris.

He took exception to the use of the term "refractive index," which he thought might convey misleading ideas.

Mr. Allen agreed with Mr. Bevan as to the usefulness of the instrument. He thought, however, that the price charged for it was a great deal too high. He had reason to believe that the angle of the prism was not strictly the same in all instruments, and this would account for some of the discrepancies to be found among the results of different operators. But a sample of lard, which showed $4\frac{1}{2}°$ in his own instrument, gave 6° in Mr. Bevan's and 11° in that of another well-known analyst, all these observations being made by Mr. Allen personally. This state of things was a disgrace to the manufacturers of the instrument.

The Chairman questioned whether the oleo-refractometer afforded any more information than could be obtained from the iodine absorption test. The figures given in the paper seemed to him to show that oils of high iodine absorption also had a high refractive power, and that the latter stood in direct proportion to the iodine absorption. If this was really the case, he thought the iodine absorption test was much to be preferred.

NOTE ON THE DETECTION OF COTTON-OIL IN LARD.

By E. B. Kenrick.

Various conflicting statements have been made regarding the absorption-spectrum of cotton-seed oil, some writers affirming that the oil gives a banded spectrum, others asserting the contrary. Some years ago, when much attention was being paid by analysts to the detection of cotton-seed oil in lard, I examined spectroscopically a number of samples of the oil. The samples included specimens obtained from American and Canadian lard manufacturers, as well as the pale yellow varieties sold as cheap salad-oil. Marked differences were observed even among samples resembling each other in outward appearance; all the samples with one exception showed, when first obtained, in layers an inch or less in thickness, a banded spectrum. In most instances the bands gradually disappeared on keeping. A sample of crude-oil, however, still showed the chlorophyll band in the red at the end of six years. The sample referred to as giving no banded spectrum was a sample of "white" oil from a Chicago lard manufacturer. It appears to be the kind commonly employed in lard compounds. When examined in thicknesses of two feet, the oil had a yellow colour, and cut off all light more refrangible than the green, but no traces of bands appeared. During the last six years I have frequently examined the absorption-spectrum of compound lards, in the hope of detecting vegetable oils by this method, but until recently I have always obtained negative results. I have now come across samples which give the chief chlorophyll band in the red, when examined in thicknesses of two or three inches.

The delicacy of the spectroscopic test will depend, of course, on the nature of the cotton-seed oil used, and the test is quite worthless for quantitative purposes. Though no conclusion as to the presence of cotton-seed oil can be drawn from negative results, on the other hand, in cases where the less highly-refined oil has been employed, a few per cents. of the oil may be detected by passing the light through a sufficiently long column of the melted fat.

St. John's College, Winnipeg.

A Modification of Renard's Process for the Detection of Arachis Oil. H. Kreis. (*Chem. Zeit.*, 1895, xix., 451-452.)—The detection of arachis oil is usually effected by means of the characteristic properties of arachidic acid. The separation of the soluble from the insoluble lead salts of the total fatty acids, by taking advantage of the difference of their solubility in ether, presents some difficulty on account of the pasty consistency which they possess. The author has mitigated this

objection by precipitating the solution of the fatty acid with an alcoholic solution of lead acetate instead of the usual aqueous liquid. The process thus worked out may be described as follows : 20 grammes of the oil are saponified with 10 c.c. of caustic soda solution (40 per cent.) and 50 c.c. of alcohol (90 per cent.). After distilling off the alcohol, the fatty acids are thrown down with hydrochloric acid, washed with hot water, and dissolved in 100 c.c. of alcohol of the strength given above. The solution is cooled in ice water, and to it is added, with constant stirring, a solution of 15 grammes of lead acetate in 150 c.c. of alcohol (90 per cent.). The precipitate, after standing for two hours, is filtered through cotton-wool by the aid of a pump, and extracted for six hours with ether. The residue is then placed in a porcelain dish, and boiled with 250 c.c. of hydrochloric acid (5 per cent.) until the fatty acids swim upon the surface as a clear oily layer. The acids thus obtained are washed two or three times with hot water to remove lead chloride, dried by pressing between filter paper, dissolved by gentle warming in 100 c.c. of alcohol (90 per cent.), and the solution cooled to 15° C. for several hours, by which process separation of arachidic acid takes place, the identification of which is effected in the usual manner.

When no special economy in ether is requisite, the process may be simplified as follows : The fatty acids obtained from 20 grammes of oil are dissolved in 300 c.c. of ether, and treated at the temperature with 150 c.c. of the alcoholic solution of lead acetate mentioned above. Lead oleate remains in solution, and the precipitate which forms after a few hours consists almost wholly of the lead salts of solid fatty acids. The precipitate is collected, washed with ether, and identified as in the previous case.

B. B.

On the Examination of Linseed Oil and Boiled Linseed Oil. F. Filsinger. (*Zeit. für angewand. Chemie*, 1895, pp. 158, 159.)—The author here replies to Dr. Amsel's criticisms on his method of examining oils with the polarimeter (see ANALYST, xx., p. 70). The dark colour of the chloroform solution of boiled oils is not of much account, since with the apparatus of Schmidt and Haensch a colourless solution is not essential. No difficulty in taking the observation will be experienced if the solution of the boiled oil be first filtered, and in many cases it is so clear that this is not required.

It is true that mineral oil is optically inactive ; but in the first place the saponification figure will detect it, and in the second place any extensive adulteration with it is unlikely, since a small addition would yield no profit, while a larger one would altogether prevent the oil from drying. There is, therefore, but little danger of its leading to erroneous conclusions with the polarimeter. It is also doubtful whether rape-oil occurs in any quantity in linseed-oils, since it is dearer than the latter. For this reason the author doubts the interpretation of the results with oil No. 10 in Dr. Amsel's second table.

C. A. M.

Estimation of Dust in Air. Karl Arens. (*Arch. Hyg.*, xxi., pp. 325-328.)—A tube 8 to 10 centimetres in length is drawn out at one end and connected with an aspirating apparatus on the principle of the bellows. A loosely-packed layer of cotton-wool 3 to 4 centimetres thick is introduced, and 200 litres of

air drawn through by means of the aspirator during half to three-quarters of an hour. Before connecting, the dry tube and wool are weighed, and after the air has been drawn through they are allowed to stand over concentrated H_2SO_4 for twenty-four hours, and again weighed, the increase in weight being calculated as dust. The following table gives the quantities found by the author in a cubic metre of air from different sources:

	Milligrammes.		Milligrammes.
Dwelling-room	—	Iron foundry (15 to 20 workmen) .	28·0
Laboratory	1·4	,, ,, (not previously used)	1·5
Schoolroom	10·0	,, ,, (few workmen) ...	12·0
Horse-hair factory	17·0	,, ,, (during interval) ...	8·0
Sago factory	17 and 15	Snuff factory	72·0
Woollen factory, picking-room ...	7·0	,, ,, before grinding ...	16·0
,, ,, cutting-room ...	20·0	Cement works (during work) ...	224·0
Flour mill	22 and 28	,, ,, (in an interval) ...	130 0

C. A. M.

The Action of Magnesia Mixture on Glass. L. L. De Koninck. (*Chem. Zeit.*, 1895, xix., pp. 450, 451.)—The formation of a deposit in magnesia mixture prepared for the determination of phosphoric acid is a familiar phenomenon, no matter what care be taken to ensure purity of the constituent substances and perfect clarity of the solution resulting from their admixture. A white flocculent deposit always appears in the reagent bottles used for containing this particular solution. The author has collected and examined the substance thus separated, and finds that it consists of small white iridescent scales saponaceous to the touch and strongly resembling powdered talc. On drying at 100° C. the substance loses 13·5—18 per cent. water, but retains its original aspect, becoming, however, excessively hygroscopic. A sample analysed has the following composition:

	Per cent.
Water at 100° C.	13·43
Water above 100° C.	17·86
Silica	32·99
Magnesia	34·80
Alumina and ferric oxide	0·87
	99·95

The substance becomes greyish on ignition, this being due to its containing a small quantity of iron. The ignited substance is no longer hygroscopic.

The author has endeavoured to determine whether the composition of the glass of the vessels in which the magnesia mixture is kept appreciably influences the character of the precipitate formed. He finds that whether the glass have soda or potash as its characteristic alkali, it exercises no influence on the composition of the precipitate, which is sensibly similar in all cases. The quantity of the precipitate formed, however, varies notably with the nature of the glass. Thus, bottles of Thüringian glass are much more rapidly and severely attacked than those made of Bohemian glass or that of Stas. In the case of the last-named material the quantity of deposit produced is quite small. For example, a bottle exposing a surface

of 90 sq. cm. caused the formation of only 0·084 grammes of precipitate during a period of twenty-seven months. B. B.

On the Estimation of Bromine in the Presence of Chlorine. W. Wense. (*Zeit. für angewand. Chemie*, 1895, Heft i., pp. 13-14.)—For the purpose of rapidly determining small quantities of bromine in the presence of much chlorine, the author proposes an indirect process. It is based on the fact that when a mixture of Cl and Br is passed through a solution of KI an equivalent of I is liberated, the quantity of which can be determined by titration. And, further, by the liberation of the I by the Br and Cl, there will be a diminution in weight in the salt in the KI solution. The amount of this can be ascertained by evaporating part of the solution. From these two data the quantities of Br and Cl can be determined.

In making the estimation the salt solution to be examined is distilled with rather more chlorine water than is required to liberate all the Br. Care must be taken that neither the salt solution nor the chlorine water contain free acid. The Cl and Br distilling over are conducted through KI solution containing a known weight of KI, any of the usual apparatus being used for the purpose. The distillation is stopped when all the Br has passed over, a point which is determined by experience. With some salt solutions it happens more speedily than with others. Thus, $MgCl_2$ solutions retain free Cl and Br much more than solutions of the alkaline chlorides. The KI solution is next made up to a definite volume, and the amount of I liberated determined by titration in an aliquot part. A second aliquot part is evaporated to dryness on the water-bath in a porcelain dish, and the residue heated for half an hour at from 160° to 180° in an air-chamber. The temperature must not reach 200°, as, according to Petersson (*Zeit. Anal. Ch.*, 1871, 362), KI then becomes partially decomposed. This will give the loss in weight, caused by the substitution of Br and Cl for I in the KI.

In calculating the results two equations are used, which are obtained from the following data:

1 mg. Br acting on the KI causes a loss of weight in the latter of 0·5866 mg.
1 mg. Cl acting on the KI causes a loss of weight in the latter of 2·5773 mg.

If I = the weight of liberated I found by titration,
D = loss of weight in the KI,
c = quantity of Cl, b = quantity of Br } absorbed by the KI solution,

then

$$(1)\quad I = c + b + d,$$
$$(2)\quad D = 0{\cdot}5866b + 2{\cdot}5773c;$$

and from these

$$c = 0{\cdot}797\ D - 0{\cdot}295\ I,$$
$$b = 1{\cdot}295\ I - 1{\cdot}797\ D.$$

Example.—A solution was made up containing 338·5 mg. KBr, 20 grammes NaCl, and 80 c.c. H_2O, and this gave for I 1175·3 mg. and for D 721 mg., from which was calculated the amount of Br = 226·4 mg., instead of the theoretical 227·3 mg.

C. A. M.

Cactus Alkaloid.—Lewin finds (*Ber. Deutsch. Bot. Gesell.*, 1894, pp. 283-290; through *R. Micro. Soc. Journ.*, 1895, p. 191) in *Anhalonium Lewinii* and some other species of Cactaceæ, a poisonous alkaloid resembling strychnine in its properties.

F. H. P. C.

The Volumetric Analysis of Chloroplatinates; the Determination of Potassium, Ammonium, Nitrogen, and Platinum. L. L. de Koninck. (*Chem. Zeit.*, xix., 1895, 301, 302.)—All methods which have been devised for the determination of potassium volumetrically are necessarily indirect, the element (usually chlorine) which is combined with the potassium being actually estimated. Thus a process exists consisting in obtaining the potassium as the chloroplatinate, igniting this salt with a reducing agent, *e.g.*, hydrogen or oxalic acid, and titrating the potassium chloride, extracted from the residual metallic platinum, by means of silver nitrate in the ordinary way. A disadvantage of this process is that the exactitude which might be attained by taking advantage of the high molecular weight of potassium chloroplatinate is sacrificed in the course of ignition, all chlorine other than that sufficient to form KCl being dissipated. Mohr has endeavoured to meet this objection by igniting with sodium oxalate instead of oxalic acid, but the method is tedious, involving neutralization of the mass after heating and before titration. The author, some time ago, published a method (*Rev. Univ. des Mines*, 1881, 9), in which the chloroplatinate is dissolved in boiling water and reduced by means of magnesium ribbon. The process is not free from error, inasmuch as an insoluble platinum compound appears to be formed, together, it appears, with some magnesium oxychloride. The substitution of magnesium powder for ribbon gives better results, but it must be noted that commercial magnesium in both forms contains an appreciable amount of chlorine which is not due to mere surface contamination, but exists in the body of the metal. In consequence of this, not only must the magnesium employed be weighed, but also care must be taken to ascertain the evenness of the distribution of the chlorine in the metal. In consequence of these drawbacks, the author has adopted the use of formic acid (already recommended by Corenwinder and Contamine, *Comptes Rendus*, 1879, lxxxix., 907), as a reducing agent. The chloroplatinate is filtered and washed in the usual manner, dissolved in boiling water, and decomposed by calcium formate, freed from chlorine by re-crystallization. The solution is heated until the platinum has fully separated and the supernatant liquor is colourless; it is neutralized with a small quantity of calcium carbonate (prepared from the nitrate), filtered, and the chlorine determined by titration with silver nitrate in the customary way. The process is equally applicable to the ammonium salt. It can also serve for the determination of nitrogen in all cases where that element can be obtained quantitatively as ammonia, and will suffice for the estimation of the platinum on the same portion as that taken for the chlorine, all that is needful being a filtration previous to neutralization. Should bromine as well as chlorine be present, no error in the determination of the potassium or ammonium will be introduced, as the process is volumetric and valid for both halogens. Chloroplatinates can be analysed in precisely the same way. Reduction of platinum by a formate is useful

in removing excess of platinum chloride from a solution containing sodium chloride from which potassium has been separated. In this case ammonium formate (best made *in situ*) is of course used. B. B.

Method of Determining Chromium in Chrome Ore. Edmund Clark. (*Journ. Amer. Chem. Soc.*, 1895, xvii., pp. 327-330).—About ·5 gramme of the finely powdered ore is fused with 25 grammes of $KHSO_4$ in a platinum crucible with a capacity of not less than 50 c.c. About forty minutes are required for the complete decomposition of the ore, and the greatest care is necessary to insure complete fusion, and to prevent loss. The fused mass is dissolved in a platinum evaporating dish by boiling gently with 35 c.c. HCl. (sp. gr. 1·20) and 25 c.c. of water. What is left in the crucible is also dissolved and added to the rest, and the liquid is heated on the water bath in a beaker till nothing but silica remains undissolved. This is filtered off and weighed.

The filtrate is rendered slightly alkaline with ammonia, the hydroxides of chromium, aluminum and iron filtered off, dissolved in HCl, reprecipitated with ammonia, and collected on the same filter. The precipitate is washed with hot water, and lime and magnesia determined in the united filtrates by any good method.

The filter containing the mixed hydroxides is transferred to a $4\frac{1}{2}$-inch porcelain evaporating dish, and oxidized by warming very cautiously with 50 c.c. of HNO_3 (sp. gr. 1·42), with the addition from time to time of small quantities of $KClO_3$. The chromium now exists as chromic acid.

The solution is transferred to a 12-oz. beaker, made up to about 150 c.c. with water, and the iron and alumina precipitated with ammonia. The precipitate is filtered, dissolved in dilute HNO_3, reprecipitated, collected and washed on the same filter, and the iron and alumina determined by any good method.

The ammoniacal solution containing the chromium as ammonium chromate is acidified with HCl, and sufficient sulphurous acid water added to completely reduce the chromium, which, after the SO_2 has been completely removed, is precipitated with ammonia, and weighed as Cr_2O_3.

Another method of determining the chromium is to moderately acidify the ammonium chromate solution with acetic acid, add an excess of clear plumbic acetate solution, allow the precipitate to settle for several hours, collect on a weighed filter, and wash with cold water. The filter is dried and weighed, and the difference in weight gives the weight of the plumbic chromate, from which the amount of chromic oxide may be calculated. C. A. M.

On a New Alkaloid in Coffee. Pietro Paladino. (*Gazzetta Chimica Italiana*, xxv., 1895, pp. 104-110.)—The author has found a new alkaloid in coffee which has physical and physiological properties quite different to those of caffeine. To this alkaloid he has given the name of "Coffearine." To obtain it the finely divided coffee is boiled with ten times its weight of water rendered alkaline with milk of lime, the boiling being repeated with successive quantities of water until the coffee is completely exhausted. The liquid strained off is filtered through linen, and basic

lead acetate added until the precipitation is complete. The precipitate is filtered off, the excess of lead in the filtrate removed by precipitation with H_2SO_4, and the clear filtrate, after being concentrated, completely exhausted with chloroform in order to extract all the caffeine.

The liquid from which the caffeine has been removed is then heated on the water bath with an excess of H_2SO_4 in order to expel all the acetic acid. The syrupy mass is taken up with water, the insoluble matter removed by filtration, and the liquid decolorized by heating on the water bath with animal charcoal.

The solution is diluted with much water, and when cold, Dragendorff's reagent is added with constant shaking, until the flocculent precipitate becomes crystalline. The precipitate is filtered off, washed, and decomposed by warming with H_2SO_4. After filtration, the liquid is warmed on the water bath, neutralized with $PbCO_3$, and again filtered. The precipitation with Dragendorff's reagent is repeated several times until the precipitate of the double iodide of the alkaloid and bismuth is perfectly crystalline.

Oxide of silver is added to the clear liquid resulting from the decomposition of the double iodide, and after filtration the hydrochloride of the alkaloid is precipitated with HCl.

The alkaloid gives no precipitate with picric acid or mercuric chloride. With tannic acid it gives a white flocculent precipitate, and with platinic chloride a yellow crystalline one.

The mean results of the analysis were :

	Found.	Calculated for Formula. $C_{14}H_{16}N_2O_4$.
C.	60·64	60·87
H.	5·74	5·80
N.	10·10	10·14

On frogs coffearine acts as a narcotic poison, 0·2 gramme proving fatal. On the other hand, as much as 0·8 gramme only produced a slight torpor in a medium-sized mouse. C. A. M.

The Estimation of Paraffin in Crude Anthracene. Fr. Heusler and Jos. Herde. (*Zeit. für angewand. Chem.*, 1895, p. 253.)—The method proposed depends on the fact that, with the exception of paraffin, all the constituents of crude anthracene are soluble in fuming nitric acid. About 2 grammes of the crude substance are weighed into a 150 c.c. flask, and 25 c.c. of fuming nitric acid added—at first drop by drop—while the flask is cooled with ice water. After the anthracene has been completely digested with the acid, the flask is warmed on the water bath until the paraffin melts. On cooling, the paraffin is filtered off on asbestos, thoroughly washed with fuming HNO_3, and afterwards with water until no longer acid. It is then washed with alcohol and warm ether into a reagent cylinder. The alcohol is poured into a weighed porcelain dish and evaporated on the water bath. Then the ethereal solution is added, the ether evaporated, and the residue of paraffin dried for half an hour at from 105° to 110° and weighed. C. A. M.

Note on the Determination of Zinc. P. W. Shimer. (*Journ. Amer. Chem. Soc.*, xvii., 1895, pp. 310-312.)—In estimating zinc in ores also containing manganese, it is usual to separate the former by precipitating it as sulphide in a solution strongly acidified with acetic acid. When the manganese is high it is necessary to dissolve this precipitate and reprecipitate it. To avoid this the following method, which gives results agreeing closely with those obtained by the usual methods, is proposed.

About ·8 gramme of the zinc ore is dissolved in HCl. When any insoluble manganese or zinc spinel is present, a fusion must be made. The HCl solution is evaporated to dryness, redissolved, and the silica filtered off, if this is to be determined. Where the silica is not required it need not be filtered off. Redissolve in HNO_3 (1·20), and evaporate to moist dryness. Add 100 c.c. of strong HNO_3, and precipitate the manganese as dioxide by $KClO_3$, as in Ford's method for manganese in iron and steel. Filter through asbestos by means of the filter-pump, and wash with strong HNO_3, followed by cold water. The manganese in the precipitate may then be determined by dissolving it in standard ferrous sulphate and titrating the excess of ferrous sulphate with standard permanganate.

The filtrate is evaporated to dryness in a beaker, a little HCl added and again evaporated to moist dryness. On this solution the usual double basic acetate precipitation is made. The united filtrates are evaporated down to about 300 c.c., heated to boiling, removed from the flame, and a rapid current of H_2S passed through for thirty minutes. The zinc sulphide is filtered off, dissolved in HCl, and the zinc precipitated preferably as zinc ammonium phosphate. The precipitate, separated from the paper, is ignited cautiously at a low red heat, and weighed as zinc pyrophosphate. If calcium is to be determined in the filtrate from the zinc sulphide, the calcium oxalate must be dissolved and reprecipitated, since the first precipitate is sure to contain considerable quantities of alkaline chlorides.

C. A. M.

Standardization of Sulphuric Acid. F. S. Shiver. (*Journ. Amer. Chem. Soc.*, xvii., 1895, pp. 351-354.)—In 1892, M. Weinig* proposed a method for standardizing sulphuric acid, in which ammonia in slight excess was added to a measured portion of the acid, the solution evaporated to dryness, and the residue dried at 115° to 120°, and weighed as ammonium sulphate. The author finds that there is a slight decomposition on evaporating an aqueous solution of ammonium sulphate to dryness. To avoid this he moistens the residue with strong ammonia water, dries on the water bath, and afterwards at 110° to 120°, till the weight is constant. The results obtained by this method agree closely with those obtained by precipitation of the sulphuric acid as barium sulphate.

C. A. M.

* *Zeit. für angewand. Chem.*, 1892, pp. 204, 205; *Analyst*, xvii., 90.

CORRESPONDENCE.

To the Editors of THE ANALYST.

Medical School, Caxton Street, Westminster,
May 27, 1895.

SIRS,—I should be greatly obliged if you could find room in the next issue of THE ANALYST for the inclosed report, which I sent to the Medical Department of the Local Government Board on November 7, 1887. A comparison of the report on the four waters from Mountain Ash, with the remarks thereon made by Dr. Thresh in his paper (ANALYST for May, p. 104, remark 17), gives an instructive illustration of the manner in which advocates of the biological examination of water deal with chemical analysis.

I can only express a hope that the other remarks of Dr. Thresh in the same paper are more fair and to the point.—Yours, etc.,

A. DUPRÉ.

[COPY.]

The waters are all soft, and leave but little dry residue. The chemical character is almost identical, as, with one or two exceptions, all the variations observed are within the limits of experimental error. Taken separately, each one of the waters must be pronounced as very pure, and free from any indications of sewage pollution.

Looking at them, however, as all coming from the same general source, there are indications pointing to a slight degree of pollution in some of the waters.

Thus, contrasting No. I. with No. Ia., it will be seen that the latter shows a little more dry residue, a minute trace (certainly a very minute trace) of ammonia not found in No. I., and a distinct increase in the proportion of phosphoric acid. In a similar manner, II. and IIa. are slightly less pure than No. I.

The nature of the deposits, however, furnishes far more marked difference. Thus, the deposit from No. I. consists almost entirely of mineral matter, oxide of iron chiefly, and contains neither fungoid growths nor living organisms.

The deposit from No. Ia. contains particles of decayed wood, vegetable fibres, and numerous large animalculæ. The deposit from No. II. shows numerous starch grains (potato ?), fungoid growths, vegetable fibres, the remains of some insect, some large and some small animalculæ. No. IIa. contains an appreciable amount of deposit, consisting mainly of oxide of iron and clay, but contains also fungoid growths, some naviculæ, and a few larger animalculæ.

Taking all points into consideration, No. I. is the most pure of the samples, while the remaining three samples show signs of pollution, indicated partly by their chemical character, more so by the character of their deposits.

(Signed) A. DUPRÉ.

November 7, 1887.

APPOINTMENT.

MR. LEO TAYLOR has been appointed Public Analyst for Hackney, in succession to the late Dr. Tripe.